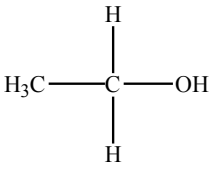
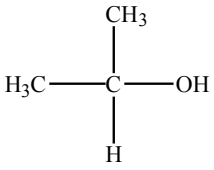
Experiment 6 – Alcohols and Phenols

Alcohols are organic molecules that contain a hydroxyl (-OH) group. Phenols are molecules that contain an –OH group that is directly attached to a benzene ring.

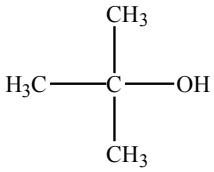
Alcohols can be classified as primary, secondary, or tertiary. This classification is based on whether the alcohol carbon is attached to one, two, or three alkyl groups. This classification is important, because the different classes of alcohols react differently. Examples of the classes of alcohols are shown below.



A primary alcohol



A secondary alcohol



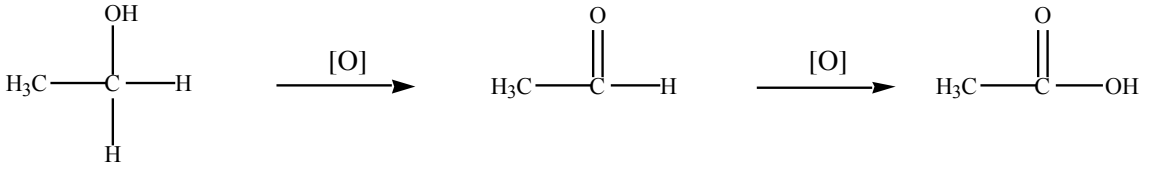
A tertiary alcohol

Because alcohols contain an –OH group, they are able to form hydrogen bonds to one another. They therefore have high boiling points. Alcohols can also form hydrogen bonds with water, so small alcohols are water-soluble. The smallest alcohols, methanol (CH_3OH) and ethanol (CH_3CH_2OH), are completely soluble in water in any proportions. As the hydrocarbon part of an alcohol gets larger, the alcohol becomes less water soluble and more soluble in nonpolar solvents.

Phenol is somewhat soluble in water. It acts as a weak acid in water, so a solution of phenol will be slightly acidic.

Oxidation

Alcohols can be oxidized by oxidizing agents such as chromate or dichromate ions (these contain chromium in the +6 oxidation state). A primary alcohol is oxidized to an aldehyde and then oxidized further to a carboxylic acid.

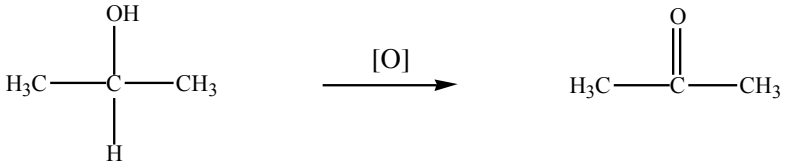


A primary alcohol

An aldehyde

A carboxylic acid

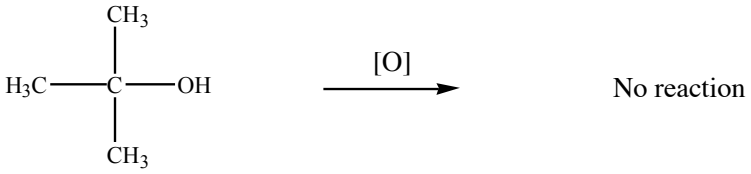
Secondary alcohols are oxidized to ketones.



A secondary alcohol

A ketone

Tertiary alcohols cannot be oxidized.

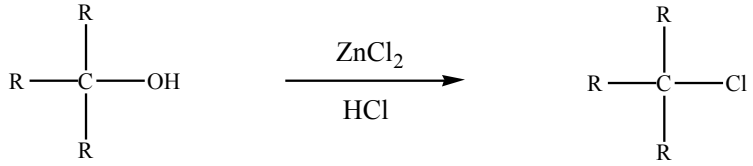


A tertiary alcohol

In the process of oxidation, the orange chromate solution is reduced to a green solution containing chromium in the +3 oxidation state. During this oxidation, hydrogen atoms are removed from the alcohol (one hydrogen is removed from the -OH group and the other is removed from the carbon atom that is attached to the –OH group). Tertiary alcohols cannot be oxidized because there is no hydrogen atom attached to the alcohol carbon. In this test, if the orange solution of chromate turns green, it is taken as evidence that oxidation has occurred. If the substance tested is an unknown alcohol or phenol and you see a positive reaction, it means that it cannot be a tertiary alcohol. Phenols can also be oxidized, but they are not oxidized to aldehydes or ketones.

Lucas Test

Some alcohols react with $ZnCl_2$ in an acidic aqueous solution to give an alkyl choride. The Lucas test involves a substitution reaction, where the –OH group of the alcohol is replaced by a Cl atom. The Lucas reagent consists of a mixture of HCl and $ZnCl_2$ that are dissolved in water.

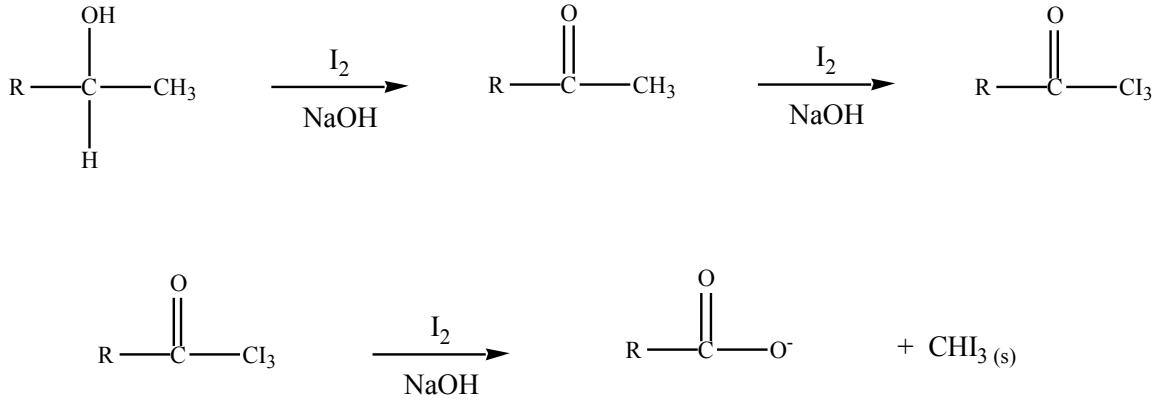


A tertiary alcohol A tertiary alkyl chloride

The mechanism of this reaction involves a carbocation intermediate: first an OH^- ion is removed from the alcohol, leaving the carbon atom in the molecule positively charged. Then a Cl^- ion adds to the positively charged carbon atom. The result is the alcohol is converted to a chlorinated alkane, with the Cl occupying the spot that the –OH was in. Since tertiary carbocations are much more stable than primary or secondary carbocations, tertiary alcohols will react readily with the Lucas reagent. Secondary alcohols will react slowly (usually in 5-10 minutes). Primary alcohols will not react much at all, since a primary carbocation is so unstable. The chlorinated product is usually insoluble in water (the solvent in this reaction), whereas the initial alcohol is usually soluble in water because of its –OH group. Cloudiness appearing in the reaction mixture is taken as evidence of a positive reaction. You will need to note the time at which the cloudiness appears.

Iodoform Test

The iodoform test is used to identify secondary alcohols that have a methyl group on the alcohol carbon. This type of alcohol will react with I_2 in NaOH to give a yellow precipitate of iodoform, CHI_3. The reaction is shown below.



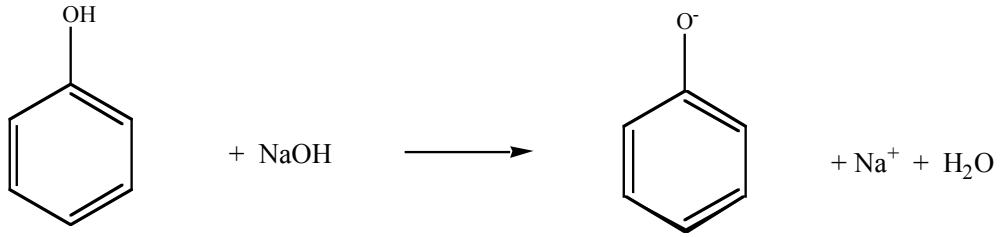
The formation of a yellow precipitate in the test solution is taken as a positive reaction, and it means that the reactant alcohol was a secondary alcohol with a methyl group on the alcohol carbon.

Iron Chloride Test

Phenols react with $FeCl_3$ to form a colored complex with the Fe^{3+} ion. The color varies from purple to orange depending on the structure of the phenol tested. Alcohols do not form colored complexes with iron ion. In this test, the appearance of a color is taken as a positive test and it indicates that a phenol was present in the original solution.

Reaction With Base

Phenols are weak acids – in water, they ionize slightly to form phenoxide ion and hydronium ion, which makes the solution acidic. Because phenols are weak acids, they will react with bases. If phenol is reacted with NaOH (a strong base), it is completely converted to the phenoxide ion, which is soluble in water because it is charged. Phenol itself is not very soluble in water. You will compare the solubility of phenol in water, in the weak base $NaHCO_{3\ (aq),}$ and in the strong base $NaOH_{\ (aq).}$.



Phenol Phenoxide ion

Safety Precautions:

- Organic compounds are extremely flammable. Use small amounts of the compounds, and do not use Bunsen burners in the organic chemistry laboratory.
- Keep the organic solvents under the fume hood.
- Avoid touching the chemicals.
- Wear your safety goggles.

Waste Disposal:

- All waste must be placed in the **organic** waste containers (which have a pink label) in one of the fume hoods.

Procedure

Part 1: Structures of Alcohols and Phenols

1. Using the molecular model kits, make models of ethanol, 2-propanol, 2-methyl-2-propanol, and cyclohexanol. Write the condensed structural formula for each of these and for phenol. Classify each as a primary, secondary, or tertiary alcohol. (Do not classify phenol in this way, because it doesn't fit any of these categories.)

Part 2: Solubility

2. You will be testing the following compounds: ethanol, 2-propanol, 2-methyl-2-propanol, cyclohexanol, 1-octanol, a 20% phenol solution, and your unknown. Label seven test tubes and place 10 drops of each compound in separate test tubes. Add about 2 mL (40 drops) of deionized water to each test tube, and shake each test tube side to side to mix. If the substance is soluble in water, you will see a clear solution with no separate layers. If it is insoluble, you will see separate layers or a cloudy solution. Record your observations.
3. Obtain seven separate dry test tubes. Again, label them and place 10 drops of each compound to separate tubes. This time, add about 2 mL (40 drops) of hexane to each tube. Shake each tube to mix. Record your observations.

Part 3: Oxidation

4. In this part, you will test the following compounds: ethanol, 2-propanol, 2-methyl-2-propanol, phenol solution, and your unknown. On a white spot plate, place 1 drop of each alcohol to be tested in separate wells. Add 5-8 drops of alcohol-free acetone to each well and stir each mixture with a thin glass rod. Make sure to rinse and wipe off the stirring rod between solutions so that you don't accidentally contaminate the solutions (this would give you ambiguous results). Add 1 drop of the chromic acid reagent to each well and stir with the glass rod (again rinsing between solutions). Observe any color change that happens within the first 10 seconds. If the orange color changes to green, reaction has taken place. Record your observations.
5. Predict the products in each case (except phenol) where a reaction occurred. If no reaction took place, write "NR".

Part 4: Lucas Test

6. In this part, you will test ethanol, 2-propanol, 2-methyl-2-propanol, and your unknown. Label 4 test tubes and place 2 drops of the liquid to be tested in its own tube. Add 10 drops of the Lucas reagent to each tube and shake the tubes to mix them. A positive test is indicated by cloudiness appearing in the tube. If no cloudiness appears within 10 minutes, place the tube(s) in a warm water bath (not boiling water) for 10 minutes. If no cloudiness appears after this amount of time, no reaction occurred. Record your observations and the approximate amount of time required for a reaction.

Part 5: Iodoform Test

7. In this part, you will test ethanol, 2-propanol, phenol solution, and your unknown. Place about 1 mL of water (20 drops) in each of 4 test tubes. Add 5 drops of the liquid to be tested. Add 10 drops of 10% NaOH and mix by shaking each tube side to side. Add 10 drops of KI/iodine solution and shake to mix. A yellow precipitate indicates a positive reaction.

Part 6: $FeCl_3$ Test

Caution: avoid skin contact with phenols!

8. You will test ethanol, solid phenol, solid salicylic acid, and your unknown. To test a solid, put a pea-sized amount of solid in a test tube and add 1 mL of water. Shake the tube to dissolve the solid as well as possible (don't worry if the solid doesn't completely dissolve). Add 1 drop of $FeCl_3$ solution and watch for a color change. A purple color indicates a positive reaction. To test a liquid, put 5 drops in a test tube and add 1 drop of $FeCl_3$ solution.

Part 7: Phenol Solubility in Base

9. Obtain 3 test tubes. Place 2 mL of deionized water in one test tube, 2 mL of 5% $NaHCO_{3\ (aq)}$ in another, and 2 mL of 5% $NaOH_{\ (aq)}$ in the third. Add 0.25 g of solid phenol to each tube. Shake each one thoroughly to try to dissolve the solid. Record the relative solubility of phenol in each of the solutions.

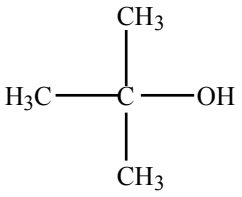
Part 8: Identification of the Unknown Substance

10. Based on the results from each of the experiments, discuss what you know about the structure of your unknown.

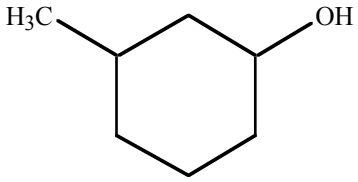
Questions

1. Label each of the following alcohols as primary, secondary, tertiary, or phenolic and name each one.

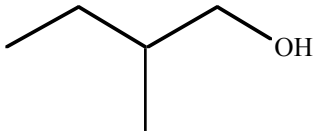
a.



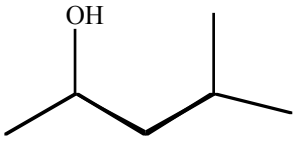
b.



c.

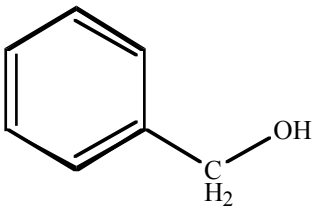


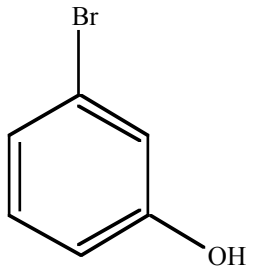
d.



e.

f.

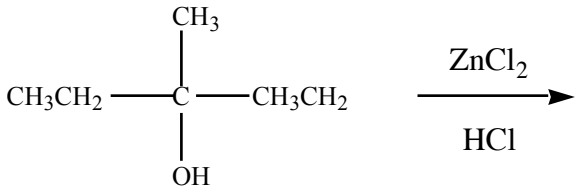


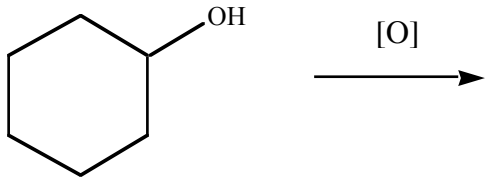


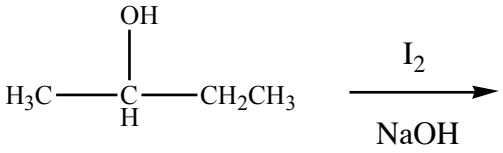
2. An unknown has a chemical formula of $C_4H_{10}O$. When chromic acid was added to the unknown, it turned green. When the Lucas reagent was added to a separate portion of the unknown, it turned cloudy in 5 minutes. When NaOH and KI/iodine was added to the unknown, a yellow precipitate formed. What is the structure of the unknown compound?

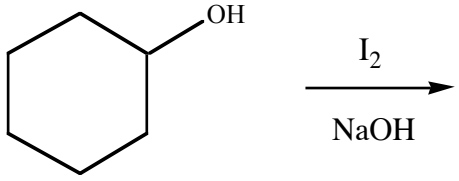
3. Write the structure of the product(s) of each of the following reactions.

a. $CH_3CH_2CH_2OH \xrightarrow[HCl]{ZnCl_2}$

b. 

c. 

d. 

e. 

4. Would you expect 1-propanol to be soluble in water? Would you expect 1-heptanol to be soluble in water? Would either of them be more soluble in hexane than in water? Explain.

5. An unknown alcohol or phenol was tested in the lab. When chromic acid was added, it turned from orange to green. When $FeCl_3$ was added to a separate portion of the unknown, it turned purple. What can you say about the structure of this unknown?